Simultaneous Determination of Palladium and Nickel in Electroplating Solutions by Differential-pulse Polarography

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Differential-pulse polarography can be successfully employed for the simultaneous determination of palladium and nickel in electroplating baths. Both palladium and nickel give peaks in ammoniacal ammonium chloride and ammoniacal ammonium tartrate media that are separated by about 250 mV. When the nickel-to-palladium ratio exceeds 100, ethylenediaminetetraacetic acid (EDTA) may be added to complex nickel and thus remove the interference due to an excess of nickel. In the presence of large amounts of palladium, dimethylglyoxime is used to enhance the peak current of nickel. The palladium peak in ammoniacal ammonium chloride buffer at pH 9.0 is not affected by the presence of either EDTA or dimethylglyoxime. Hence it is possible to determine palladium and nickel simultaneously and in the presence of an excess of each other.

Keywords: *Palladium determination; nickel determination; differential-pulse polarography; dimethylglyoxime; electroplating solution*

Electroplating baths containing various amounts of palladium and nickel are used for the deposition of certain alloy compositions. Recently, palladium–nickel alloy coatings have gained acceptance as an undercoat to reduce the thickness of gold plating in the electronics and watch industries. These alloys are used as a substitute for gold as a contact material for electronics applications. There are economical and technological advantages for substituting palladium or palladium alloys for gold.[1] Economically, substantial cost reductions can be achieved owing to the lower price of palladium coupled with its lower density. Technologically, material properties of palladium such as hardness, ductility and thermal stability are superior to those of hard gold. The use of palladium–nickel alloy plating is increasing and hence it is necessary to determine the palladium and nickel contents in plating solutions, wash solutions and effluents.

Both palladium and nickel form coloured complexes with dimethylglyoxime (DMG) and this has been employed for the separation of palladium from other elements,[2] but as the sensitivity of the palladium–DMG complex is low, it is rarely used for its determination.[3] We have found that by using differential-pulse polarography (DPP), it is possible to determine palladium and nickel simultaneously and the method does not involve any tedious and time-consuming separation steps.

Wild[4] used a supporting electrolyte (SE) of 1 mol dm^{-3} pyridine and 1 mol dm^{-3} potassium chloride for the determination of Pd^{II} in nickel and palladium plating solutions. Other supporting electrolytes used are cyanide,[5] ethanolamine,[6] glycine[7] and caprolactam,[8] but it was not reported whether these media could be used for the simultaneous determination of nickel and palladium. Flora and Nieboer[9] investigated the highly sensitive peak obtained for Ni^{II} in the presence of DMG and applied this method to the determination of Ni^{II} in lake water by DPP. Later, Torrance[10] used this method for the determination of Ni^{II} and Co^{II}. This paper describes polarographic methods for the simultaneous determination of nickel and palladium in electroplating baths, effluents and wash solutions.

Experimental

Apparatus

Polarograms were recorded with a Model CL-90 pulse polarograph [Elico(p), Hyderabad, India] in conjunction with a Metrohm polarographic cell; with a dropping mercury electrode (DME) as working electrode and a mercury pool as counter electrode. A saturated calomel electrode (SCE) was used as the reference electrode and was connected to the polarographic cell *via* a potassium chloride–agar bridge. A Sargeant capillary with a natural drop time of 3 s was employed as the DME. The drop time was mechanically controlled. For DPP measurements, the pulse duration was 40 ms and the pulse amplitude was 50 mV. Purified nitrogen was used for de-aeration of the solution.

Reagents

All reagents were of analytical-reagent grade. A standard solution of palladium (1 mg cm^{-3}) was prepared by dissolving pure $Pd(NH_3)_2Cl_2$ in a sufficient volume of ammonia solution (1 + 1) and diluting to volume. A standard solution of nickel (1 mg cm^{-3}) was prepared by dissolving high-purity nickel powder in dilute nitric acid. A 1% solution of DMG in ethanol was used. Ammonium tartrate–ammonia and ammonium chloride–ammonia buffers (pH 9.0) were prepared.

Recommended Procedure for the Simultaneous Determination of Palladium(II) and Nickel(II)

Transfer a suitable aliquot of the sample solution into the polarographic cell and add 10 cm^3 of 0.2 mol dm^{-3} ammoniacal ammonium chloride buffer (pH 9.0). Pipette 0.2 cm^3 of DMG solution and dilute to 20 cm^3. De-aerate the solution and record the polarogram from −0.50 to −1.20 V *versus* SCE. Calculate the Pd^{II} and Ni^{II} concentrations in the sample by the standard additions methods.

Results and Discussion

Choice of Supporting Electrolyte

Table 1 gives the sensitivity values for Pd^{II} and Ni^{II} in the various SEs employed. The DPP conditions used were drop time = 0.5 s and pulse amplitude = 50 mV. Buffers containing 0.1 mol dm^{-3} ammonium chloride or 0.1 mol dm^{-3} ammonium tartrate at pH 9.0 ± 0.1 were used. It was found that either ammoniacal ammonium chloride or ammoniacal ammonium tartrate could be employed for the simultaneous determination of Pd^{II} and Ni^{II} as their peaks are well separated in both media. The sensitivity of Pd^{II} was almost the same in both supporting electrolytes whereas the sensitivity of Ni^{II} was higher in 0.1 mol dm^{-3} ammoniacal ammonium chloride

Table 1 Sensitivities for Pd^{II} and Ni^{II} in different SEs. DPP conditions: drop time = 0.5 s; ΔE = 50 mV; m = 1.84 mg s^{-1}

Supporting electrolyte	Sensitivity/nA (ppm)$^{-1}$ Pd^{II}	Ni^{II}
0.1 mol dm^{-3} NH_4Cl (ammoniacal) (pH 9.0)	40	110
0.1 mol dm^{-3} ammoniacal ammonium tartrate (pH 9.0)	39.2	85
0.1 mol dm^{-3} NH_4Cl (ammoniacal) (pH 9.0) + 0.01 mol dm^{-3} EDTA	42	0
0.1 mol dm^{-3} NH_4Cl (ammoniacal) (pH 9.0) + 0.01% DMG	38	1200
0.1 mol dm^{-3} ammoniacal ammonium tartrate (pH 9.0) + 0.01% DMG	36.8	1150

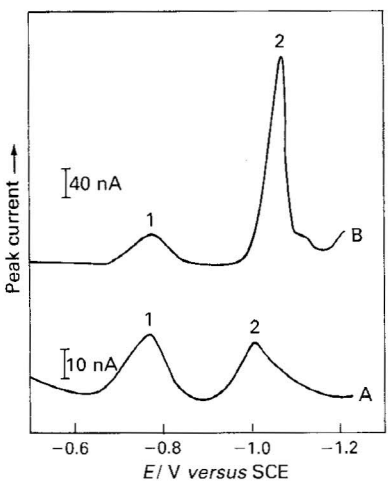

Fig. 1 Differential-pulse polarograms of Pd^{II} and Ni^{II} in ammoniacal ammonium chloride buffer with and without DMG. t = 0.5 s; ΔE = 50 mV. A, $[Ni^{II}]$ = 0.20 ppm and $[Pd^{II}]$ = 0.50 ppm. B, $[Ni^{II}]$ = 0.20 ppm, $[Pd^{II}]$ = 1.0 ppm and [DMG] = 0.01%

buffer. When the nickel concentration is very low, addition of DMG enhances the peak height of nickel. The sensitivity of Ni^{II} in the presence of DMG was comparable in both ammoniacal ammonium chloride and ammoniacal ammonium tartrate media. Addition of a small volume of 0.1 mol dm^{-3} ethylenediaminetetraacetic acid (EDTA) results in the complete removal of the nickel peak owing to complexation. The sensitivity of Pd^{II} was not affected by the presence of EDTA. Typical polarograms of Pd^{II} and Ni^{II} in 0.1 mol dm^{-3} ammonium chloride buffer (pH 9.0 ± 0.1) with and without DMG are given in Fig. 1.

The blank value for Ni^{II} in the presence of DMG in ammoniacal ammonium chloride buffer was lower than that in ammoniacal ammonium tartrate buffer. Therefore, it was preferable to use 0.1 mol dm^{-3} ammoniacal ammonium chloride buffer with DMG.

Hence it can be seen that although Pd^{II} also forms a complex with DMG, it does not interfere in the determination of Ni^{II}. Unlike nickel, there was no enhancement of the peak current for Pd^{II} in the presence of DMG. This allowed the determination of trace amounts of nickel in the presence of a large excess of palladium. Palladium(II) gave well-developed peaks in both ammoniacal ammonium chloride and ammoniacal ammonium tartrate media and these peaks were separated from the nickel peaks by about 250 mV.

Effect of Variation of DMG on the Peak Current of Nickel(II)

Fig. 2 shows the effect of varying the DMG concentration on the peak current of Ni^{II} in 0.1 mol dm^{-3} ammoniacal ammonium chloride buffer (pH 9.0 ± 0.1). A 15-fold molar

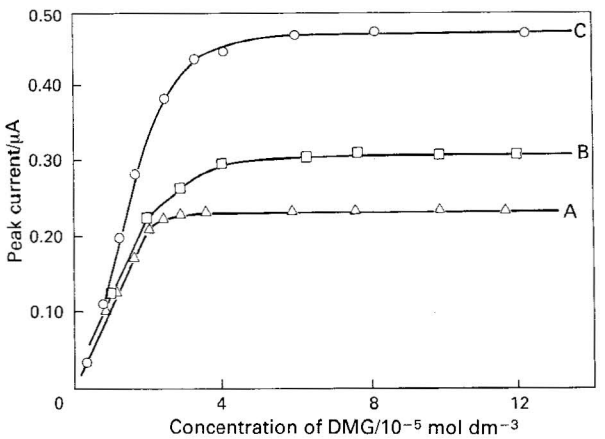

Fig. 2 Dependence of peak current on the concentration of DMG. Experimental conditions: SE = 0.1 mol dm^{-3} ammoniacal ammonium chloride buffer (pH 9.0); t = 0.5 s; and ΔE = 50 mV. Ni^{II} concentration: A, 0.16; B, 0.23; and C, 0.40 ppm

excess of DMG was sufficient to bring about the maximum peak current. This was found to be true at three different concentrations of Ni^{II}, as shown in Fig. 2. The nickel concentrations employed for this study were 0.16, 0.233 and 0.40 ppm. Flora and Nieboer[9] used a 1520-fold excess of DMG in ammoniacal citrate buffer (at a nickel level of 50 ppb) to achieve the maximum peak current. Torrance[10] also reported a 250–500-fold molar excess of DMG for the determination of 10 ppb each of Ni^{II} and Co^{II} in ammoniacal ammonium tartrate buffer (pH 8.7). We found that the amount of DMG required to give the maximum peak current for Ni^{II} was much lower in ammoniacal ammonium chloride buffer. The slightly higher DMG concentration in citrate and tartrate media must be due to the competition between the buffer components and DMG for nickel ions, as Ni^{II} forms fairly strong complexes with citrate and tartrate. As the formation constant of the $Ni(DMG)_2$ complex was high (log β = 17.24), complete complex formation could be expected to occur at a relatively low ligand-to-metal ion ratio in the absence of other complexing agents. A large excess of reagent was not favoured from a solubility point of view as the nickel–DMG complex was sparingly soluble and the solubility decreases in the presence of an excess of DMG. Hence it was possible to obtain the maximum peak current at a much lower ligand-to-metal ratio when ammoniacal ammonium chloride buffer (pH 9.0) was used.

Effect of Nickel(II) Concentration on Peak Current

In an SE of 0.1 mol dm^{-3} ammoniacal ammonium chloride at pH 9.0 and a DMG concentration of 9.38×10^{-4} mol dm^{-3}, the nickel concentration was varied and the peak currents were measured. The results are shown in Fig. 3. The peak current was found to be a linear function of nickel concentration only up to 0.5 ppm. A least-squares fit of the data was carried out by y-residual minimization and it was found that there is good linearity up to 0.50 ppm (as indicated by a correlation coefficient of 0.9995) with a slope of 1118.4 nA (ppm)$^{-1}$ and an intercept of 45.54 nA. The y-intercept corresponds to about 0.04 ppm of nickel, which results from nickel impurity in the supporting electrolyte. When the nickel concentration was increased above 0.50 ppm, the deviations from linearity became significant and at concentrations above 1 ppm the peak current decreased, as shown in Fig. 3. This could be due to precipitation of the nickel–DMG complex. The log K_s value for the equilibrium $Ni(DMG)_2(aq) \rightleftharpoons Ni(DMG)_2(s)$ was 5.68.[11] Therefore, the solubility of the complex under equilibrium conditions was $10^{-5.68}$. When the nickel concentration was increased above 1 ppm, precipitation of $Ni(DMG)_2$ began, resulting in a decrease in peak current.

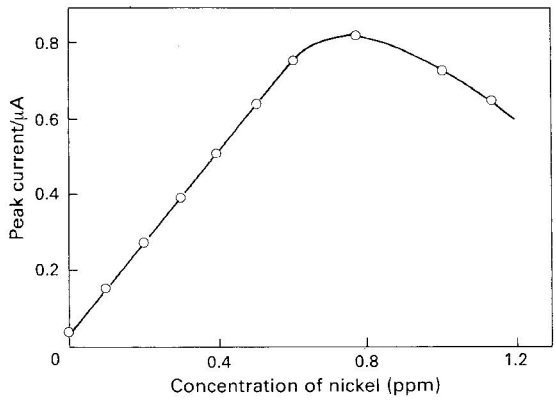

Fig. 3 Dependence of peak current on Ni^{II} concentration at a constant excess of DMG. SE and DPP conditions as in Fig. 2; [DMG] = 0.01%

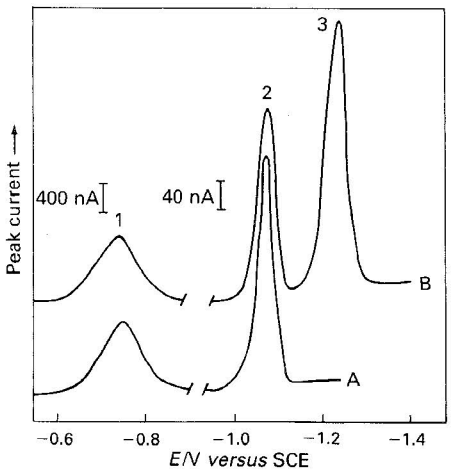

Fig. 4 Effect of Co^{II} on the adsorption peak current of Ni^{II} in the presence of DMG. A, $[Pd^{II}]$ = 25.0 ppm; $[Ni^{II}]$ = 0.25 ppm; [DMG] = 0.01% and B, $[Co^{II}]$ = 0.45 ppm; $[Pd^{II}]$, $[Ni^{II}]$ and [DMG] as in A

It was reported earlier by Flora and Nieboer[9] that the analytical application of the DMG-sensitized reaction was limited to very low nickel concentrations, as the calibration graph was linear only at Ni^{II} concentrations <100 ppb. This was true for tartrate and citrate media. However, the calibration graph was linear up to 500 ppb in ammoniacal ammonium chloride buffer (pH 9.0).

Effect of Foreign Ions

The effect of other metal ions expected to be present in electroplating baths on the simultaneous polarographic determination of Pd^{II} and Ni^{II} was investigated. It was found that comparable amounts of copper(II), iron(III), lead(II) and zinc(II) did not interfere with the simultaneous determination of Pd^{II} and Ni^{II} in an SE containing 0.1 mol dm^{-3} ammoniacal ammonium chloride buffer and 0.01% DMG. The peak current of the nickel–DMG complex was decreased by about 20% in the presence of almost double the amount of cobalt (Fig. 4).

Sensitivity and Detection Limit for Palladium(II) and Nickel(II) by DPP

It was found that the DMG enhancement factor for Ni^{II} increased as the drop time increased. Therefore, a drop time of 2 s was employed in order to obtain a higher sensitivity. The slopes of the calibration graph at a drop time of 2 s were 5350 and 80 nA μg^{-1} cm^3 for Ni^{II} and Pd^{II}, respectively.

The detection limit is defined as the concentration of the analyte resulting in a signal three times the standard deviation of the blank, as recommended by IUPAC.[12] The detection limits were about 10 ng cm^{-3} for Ni^{II} and 0.10 μg cm^{-3} for Pd^{II}. An even lower detection limit could be achieved for Ni^{II} provided that there was no contamination. However, often there was a blank due to the nickel impurity present in the SEs even when highly pure reagents were used. We found that the blank value for ammoniacal ammonium chloride buffer was less than that for ammoniacal ammonium tartrate buffer. The other advantages of ammoniacal ammonium chloride buffer were the relatively low DMG concentration required for maximum peak current and the wider linear calibration range for Ni^{II}.

Table 2 Determination of palladium and nickel in synthetic sample solutions

Sample no.	Amount added/μg		Amount found/μg		Error (%)	
	Pd^{II}	Ni^{II}	Pd^{II}	Ni^{II}	Pd^{II}	Ni^{II}
1	10.0	10.0	9.86	9.82	−1.4	−1.8
2	10.0	100.0	9.90	98.8	−1.0	−1.2
3	10.0	1000.0	9.85	985.0	−1.5	−1.5
4	100.0	10.0	99.5	9.85	−0.5	−1.5
5	200.0	5.0	198.5	4.95	−0.75	−1.0
6	200.0	2.0	198.5	1.98	−0.75	−1.0

Determination of Palladium(II) and Nickel(II) in Samples

Samples of electroplating solutions containing 10.8 g dm^{-3} of Pd^{II} and 5.0 g dm^{-3} of Ni^{II} were analysed using these DPP procedures. The DPP measurements were made in the absence of DMG as the concentrations of Pd^{II} and Ni^{II} were high in this sample. The standard deviations for six replicate measurements were found to be 0.13 for 10.77 g dm^{-3} palladium and 0.07 for 4.98 g dm^{-3} nickel.

Synthetic solutions containing ppm levels of Pd^{II} and Ni^{II} in different ratios were analysed. The DMG-sensitized procedure was used at low concentrations of nickel. The results are summarized in Table 2. It was found that this procedure permits the simultaneous determination of palladium and nickel in the presence of a 100-fold excess of the other.

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Paper 2/01286C
Received March 10, 1992
Accepted May 27, 1992